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Nitrogen-Induced Effects on Internal Stress and Adhesion Strength of Diamond-like Carbon Coating on Pure Titanium Surface

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Abstract: Diamond-like carbon (DLC) coating on pure titanium surface was prepared using pulsed arc ion plating method under the circumstance with nitrogen at different levels. By using scanning electron microscope, the surface morphology and EDS composition analysis were performed on the thin film prepared. The influence on the thickness and hardness of film imposed by nitrogen was analyzed comparatively using micro-indentation instrument. The results indicate that the nitrogen content in the film increases as the nitrogen/methane ratio in process increases. After doping nitrogen in DLC films, the microstructure of the films is altered, generating nanoparticles at the scale of few tens nanometer. Those nanoparticles possess nitrogen-rich amorphous carbon nitride CN*x* structure identified by SEM and XPS analysis. The dense DLC/CN*x* nano-composite structure reduces the internal stress of the film, thus improving the adhesion of the film on the substrate.

Key words: pure titanium; diamond like carbon; surface modification; indentation experiments

Pure titanium has been widely used as an ideal denture scaffolds in prosthodontics. Because of the limitation of casting process, there are, however, some defects such as poor wear resistance, metal ion precipitation and broken snap ring, etc., which needs to be solved by modifying the titanium surface. The diamond like carbon (DLC) had found extensive applications in industries since 1960s as new industrial materials, but has relatively few applications in prosthodontics, due to its intrinsic issues, such as high internal stress, low adhesion strength, and it is easy to exfoliate, etc[1, 2]. During the process of doping nitrogen in DLC film, it is found that the internal stress decreases with the increasing nitrogen content while the adhesion strength between DLC film and substrate materials is improved. Mikami et al[3] supposed that the cause is the decreasing content of hydrogen in DLC film. Franceschini et al[4] pointed out that the decreasing internal stress of film as doping nitrogen in DLC film should be attributed to the substitution of sp^2 carbon bond with sp^3 nitrogen bond in DLC film. In this work, we mainly study the influences on microscopic structure of DLC film imposed by nitrogen and their correlations to stress and adhesions of film.

1 Experiment

Twenty pieces of wax models were prepared, degreased by ethanol, embedded using zirconia internal embedding material and phosphate external embedding material (Dentsply, USA), and finally used for casting pure titanium (TA2, Baoji nonferrous metals processing plant) specimen. The measured thickness of internal micrometer reached 10 mm. Then it was subjected to ultrasonic cleaning and dried. The nitrogen-infiltration DLC(DLC-N) film was synthesized through chemical vapor deposition using plasma coater (УвНи ⅡA-1-001, Russia). Specimen should be subjected to ether mixture cleaning and ultrasonic cleaning before entering the vacuum chamber. As the vacuum reached 5×10^{-3} Pa, nitrogen was filled for cleaning and the specimen was heated for 30 min (at 30～60 ℃). By connecting to the DC arc titanium ion source, methane was filled through gas-phase ion source with pressure up to 150 Pa; then carbon ion source started to deposit DLC films. The working electrical voltage at 200 V, working frequency at 3 Hz, distance at 270 mm, incident angle controlled within 30° and the time over 20 min were the basic conditions. The reaction pressure was kept at 1.3 Pa for the doping system by controlling the flow rate of nitrogen gas. By fixing the flow rate of methane (10 ml/min), the flow rate of

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nitrogen can be maintained within 0-100 ml/min. The specimens were divided into four groups according to the flow rate ratio between nitrogen and methane: group A refers to ratio of 0, i.e. without adding nitrogen; group B refers to ratio of 0.15; group C refers to ratio of 1.0; group D refers to ratio of 5.0.

The X-ray photo-electron spectroscopy (JSM-6301 type X-ray spectrometer, UK, LEO Co., Ltd) was employed to determine the content of nitrogen in film. Scanning electron microscope (SR-20 type SEM, Netherland, Philips, Co., Ltd) was used to observe the surface morphology and structure of film. The Micro-indentation instrument (I1000, US) was adopted for detecting the surface indentation, observing and analyzing the variation of internal stress and adhesion strength of film.

2 Results and Discussion

In Table 1, we list the measured and observed results of nitrogen atoms percentage in film, film thickness, microscopic hardness and film adhesion strength during the synthetic process of nitrogen infiltration DLC film as the nitrogen/methane flow rate ratio changes. The nitrogen content was calculated from XPS measurements. The results indicate that nitrogen content increases as the nitrogen/methane flow rate ratio increases and tends to saturate. The thickness of film is about 1.2-1.5 μm while the microscopic hardness is averaged from three different measurements, during which the load is 5 g and indentation shape is regular. The adhesion strength is estimated with 25 g load.

As the nitrogen content increases, the microscopic hardness of DLC film decreases slightly, implying that the mechanical property of film is maintained. However, as shown in Fig.1 the stability and adhesion strength of the film increase dramatically with the increasing amount of nitrogen. This observation can be explained using the Marshall's[5,6] theory on indentation analysis of film stress. According to Marshall, there emerges a larger and circular fracture layer neighboring the film surface indentation, under certain loading. The relationship among fracture radius R, load P and internal stress σ is as follows:

$$R^2=P^2\ [(1+\nu)/2-(1-\alpha)\ \ (1-P^{-1})^2]/(1-\sigma) \tag{1}$$

Where α=0.383, ν=1/3 referring to Poisson factor, R, P and σ (varied within 0-1) are standardized variables.

$$P=C\ \ (P/Ht^2)^{3/2} \tag{2}$$

Where C is a geometric constant, H refers to microscopic hardness, and t is film thickness. From equation (2), standardized load is a constant P_c if the same load P is applied while film hardness and thickness remains fixed. Then equation (1) can be reduced to:

$$R=\ [A/(1-\sigma)]^{1/2} \tag{3}$$

Where $A=P_c^{\,2}[(1+\nu)/2-(1-\sigma)\ (1-P_c^{\,-1})^2]$ is a constant. Equation (3) gives the correlation between fracture radius R and film internal stress σ.

Table 1 The adhesion strength related mechanical properties of DLC and DLC-N films

	Flow rate ratio	N content/at%	Thickness/μm	Hardness/kg·mm^{-2}	Adhesion strength load as 25g
A	0	0	1.4	1783	Easy to broken (Fig.1-3-6 d)
B	0.15	3.4	1.2	1580	Relatively stable (Fig.1-3-6 c)
C	1.0	9.8	1.2	1370	Stable (Fig.1-3-6 b)
D	5.0	9.6	1.3	1400	Stable (Fig.1-3-6 a)

In Fig.1, the group with 0% nitrogen shows apparent fracture extending laterally around the indentation; while the fracture gradually decreases until disappears as the nitrogen content increases, demonstrating that the presence of nitrogen reduces the film layer stress and enhances the film layer toughness. The pressure resistance and hardness of DLC film groups with 9.6% nitrogen and 9.8% nitrogen are larger than that of groups with 3.4% nitrogen and 0% nitrogen. The group with 0% nitrogen shows apparent fracture extending laterally around the indentation. The group with 3.4% nitrogen has also fractures but proliferates less than 1% nitrogen group. For group with 9.6% nitrogen, there is no significant fracture around the indentation.

In order to prove the relationship between internal stress, adhesion strength and microscopic structure of DLC film with nitrogen, we investigated the samples with SEM and XPS. In Fig.2 the surface morphology of DLC film with different nitrogen contents are presented. From Fig.2, the internal crystallization of the film is not significant with nitrogen content of 0: scaly surface, more dispersed crystals and larger distance between the cross-section of pillars. As the

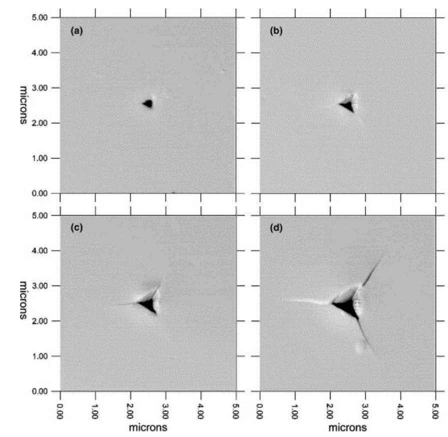

Fig.1 Microscope images of Vickers hardness indentation Nitrogen content: (a) 9.6%, (b) 9.8%, (c) 3.4%, and (d) 0%

nitrogen content increases, the larger amorphous grains on DLC film surface accumulate and transform into fine and dense crystal grains. With more nitrogen added, there appear some particles protruding over the homogeneous film surface. The density of particles increases with the increasing nitrogen and the scale of particle decreases from hundreds of nanometer down to tens of nanometers. As shown in Fig.2d when the nitrogen saturates, burr-like crystals appear on the surface, the crystal spacing at cross-section almost disappear, and the crystal pillars pack densely. The film cross section thickness increases gradually with the increasing nitrogen content. The DLC crystal pillars growing from TiN transition layer evolve from the loose into the dense structure with fine crystal diameter. The nanoparticles on sample surface gradually become fine, indicating that the internal stress approaches stable. The nitrogen free DLC film consists of homogeneous hydrogen-containing carbon grains at the scale of a few hundred nanometers. As shown in Fig.2, there still exist gaps and apertures among particles. In terms of chemical bonds, the

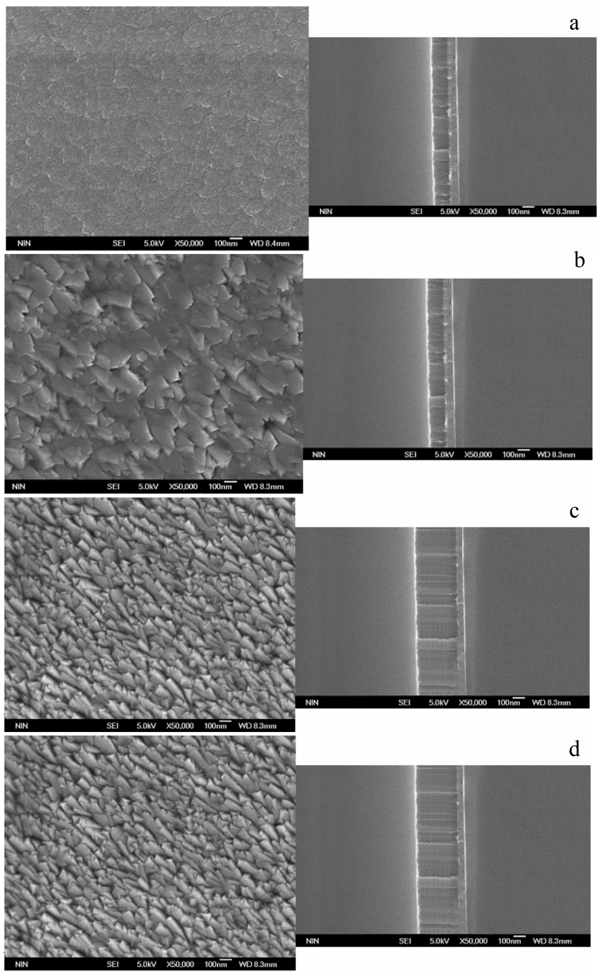

Fig.2 SEM images of surface and cross section of 9.6% nitrogen-containing DLC film: (a) 0%, (b) 3.4%, (c) 9.8%, and (d) 9.6%

DLC film consists mainly of sp^2- and sp^3-bond carbon and hydrocarbons. Due to the large difference between atomic radius of carbon and hydrogen, the sp^2 and sp^3 bonds are distorted, thus inducing large internal stress in the film. As the internal stress accumulates, fractures can be easily formed in the film and lead to broken ultimately. Or the film can be broken under external forces.

By introducing and increasing the nitrogen content, in the DLC film there emerge nanoscale amorphous CN_x particles and formulate DLC/CN_x nano-composite structure, which renders dense microscopic structure of the DLC film and eliminates essentially the apertures and cracks, as shown in Fig.2d. On the other hand, the atomic radius of nitrogen and carbon are quite close, and the lattice distortion induced by CN bond is much less than that induced by CH bond in the sp^2 and sp^3 amorphous film. Therefore, the source of partial internal stress can be eliminated in the film, reducing internal stress and enhancing the adhesion strength. Plenty of studies indicate that the defects could lead to decreasing stress in the DLC film.

Tian-ying Li[7] studied the thickness and stress relationship of the film prepared using sputtering method and proposed a structural model, in which the defect are considered as the main mechanism for releasing stress. Hence the nitrogen-containing DLC film also allows relax of the film to release strain and reduce internal stress. The trend that internal stress varies with N_2 content is similar to the variation of defects in the film. This indicates that the increasing N_2 concentration is the major cause for the reduction of internal stress of DLC film containing nitrogen. Considering the nitrogen addition effects on C-N film bond, the substitution of carbon with nitrogen reduces the average coordinate number thus lowering the extent of excessive restriction and internal stress in the film. As the nitrogen atom combines with carbon atom forming C-N bond, all valence electronic configuration of nitrogen saturates, leading to the formation of terminal bond in the network by nitrogen atom, which diminishes the sp^2 network cross-linking and reduces the internal stress.

In Fig.3 the detection depth of XPS is 10 nm. The binding energy of C1s in 9.6% nitrogen containing DLC film peaks at 285.5 eV, which lies within the energy range of carbon in DLC film. In Fig.4, the XPS probes the formation of C-N single bond in DLC film. The concentration of nitrogen decreases from the substrate to the surface.

In Fig.3, X-ray photoelectron spectrum (XPS) shows CN and CNH bonds. It might be assumed that the structure of nanoparticles is nitrogen-rich amorphous structure, distinctive from DLC. The detection depth of XPS is 10 nm. The binding energy of C1s in 9.6% nitrogen containing DLC film peaks at 285.5 eV, which lies within the energy range of carbon in DLC film. In Fig.4, the XPS probes the formation of C-N single bond in DLC film. The concentration of nitrogen decreases from the substrate to the surface. The x value of CN_x can be estimated above 0.126 from the contents of nitrogen in film.

The existence of amorphous carbon nitride nanostructure improves the structural denseness of DLC film and enhances the mechanical properties of the film[12,13].

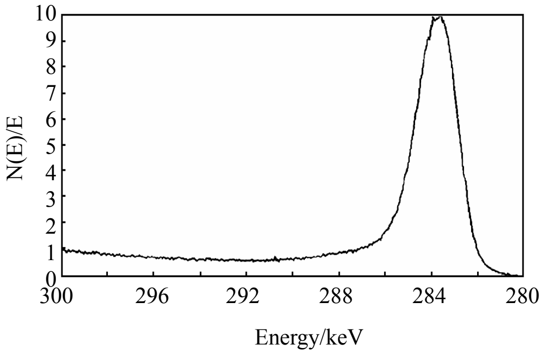

Fig.3 The C1s at 285.5eV in DLC film probed by XPS

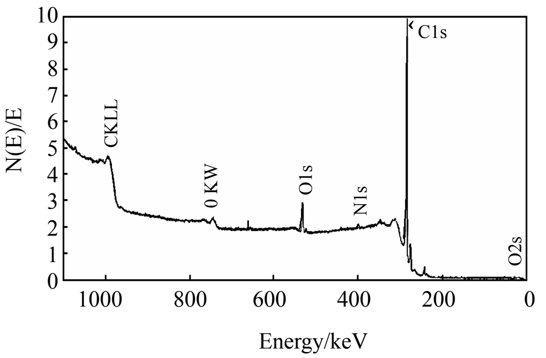

Fig.4 The formation of C-N bond in DLC film probed by XPS

3 Conclusions

1) With the increasing nitrogen/methane ratio in process, the content of nitrogen increases in the film.

2) After doping nitrogen in DLC film, the microscopic structure of the film is altered and particles at the scale of few tens nanometer are generated.

3) The SEM and XPS analysis indicate the nanoparticles has nitrogen-rich amorphous CN_x structure

4) The dense DLC/CN_x nano-composite structure reduces the internal stress of film and improves the adhesion of the film on the substrate.

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氮对纯钛表面类金刚石薄膜内应力与附着力的影响

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摘 要：采用脉冲电弧离子镀膜法于不同氮含量条件下在纯钛表面制备类金刚石膜（DLC）。利用扫描电镜观察分析不同氮含量下薄膜的表面形貌及能谱分析薄膜成分，显微压痕仪对比分析不同氮含量对薄膜厚度和硬度的影响。试验结果表明随工艺中氮气/甲烷比值的增大，薄膜中氮含量随之增大。氮掺入 DLC 薄膜后，改变了薄膜的微观结构，产生几十纳米量级的颗粒。SEM、XPS 分析表明纳米颗粒是富氮的非晶氮化碳 CN_x 结构。DLC/CN_x 致密的纳米复合结构，减小了薄膜的内应力，提高了薄膜对衬底的附着力。

关键词：纯钛；类金刚石；表面改性；压痕实验

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